

New HiTempThermo Website Provides Scientists with Thermochemical Databases and Models for High-Temperature Materials Processing, Combustion, and Corrosion

A new online database designed to provide thermochemical data for gas- and condensed-phase species relevant to a wide range of high-temperature processes is now available at <http://www.ca.sandia.gov/HiTempThermo/index.html>. The new database provides information for combustion, chemical vapor deposition (CVD), catalysis, materials corrosion, and aerosol processing applications. This dynamic website provides essential data for scientists studying high-temperature processes.

The HiTempThermo website is a much-needed resource because although thermochemical data is essential in determining the potential for chemical interactions for many chemical systems, it is often either inaccurate or nonexistent. And since the experiments that produce such data are very rare, computational techniques are often the only source of accurate data for developing quantitative process models.

The website is divided into two sections: gas-phase data and condensed-phase data. The overall organization is shown in Figure 1. The current gas-phase portion of the database includes approximately 400 compounds in the C-H-O-N-Al system relevant to combustion modeling. Additional data for compounds containing other elements, including boron and silicon, will be added in the near future. The data available for each molecule include coefficients for CHEMKIN kinetic modeling, enthalpy, free energy, entropy at 298 K, and a calculator to determine these properties at other temperatures. In addition, vibrational frequencies, spatial coordinates, moments of inertia, and electronic energies obtained from the ab initio calculations can be obtained. A free three-dimensional molecular viewing software package, MOLEKEL, is available to assist the user. Condensed-phase data currently available cover compounds in the Na-Al-B-Si-O system and can be downloaded in the form of a file that is readable by ChemSage and FactSage, which are both commonly used thermodynamic equilibrium codes.

The information provided in this database is derived from two sources: quantum-chemistry calculations for gas-phase species and the associate species model for condensed-phase species. The molecular properties available in the HiTempThermo database and in the gas-phase database are obtained from bond additivity correction (BAC) calculations, a class of quantum-chemistry-based methods developed by C.F. Melius, in collaboration with P. Ho and M.D. Allendorf. The BAC methods are based on the assumption that errors in electronic energies obtained from ab initio calculations are due to the finite size of the basis sets used and the application of limited electron correlation in the calculations. These errors are therefore systematic and correctable by applying a variety of empirical corrections related to the elements and bonds in the molecule. Predicted heats of formation from this method are typically accurate to $\pm 3 \text{ kcal mol}^{-1}$.

Computational methods for condensed-phase compounds cannot predict data with sufficient accuracy for modeling purposes. Although data for crystalline compounds are often available, data for glasses and variable-composition liquids are rarely available since their properties are strongly influenced by non-ideal-solution effects. To obtain data for glasses and liquids, a modified associate species approach is used to account for non-idealities. This relatively simple technique treats liquids as ideal solutions of end-member and associate species. The model was extended to represent glasses by treating them as supercooled liquids. Equilibrium calculations using the model allow determination of species activities, phase separation, precipitation of crystalline phases, and volatilization. This model was originally developed by Karl Spear of Penn State and Ted Besmann at Oak Ridge National Laboratory to support nuclear waste glass development. Allendorf and Spear recently applied this technique to corrosion of refractories in glass-melting furnaces.

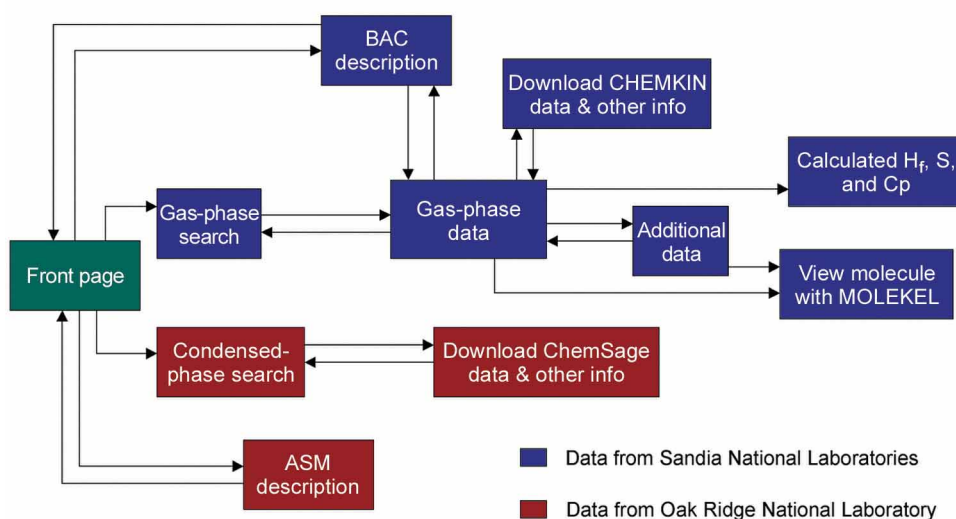


Figure 1. The HiTempThermo website is organized to provide users with straightforward entry to high-temperature gas- and condensed-phase data from the front page. Outputs include coefficients for CHEMKIN kinetic modeling, enthalpy, free energy, and entropy. Vibrational frequencies, spatial coordinates, moments of inertia, and electronic energies obtained from ab initio calculations can also be obtained. MOLEKEL is also available for three-dimensional viewing.

fraction, and temperature in turbulent jet flames. The experimental configuration for these measurements is shown in Figure 2. The forward reaction rate of the reaction $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$ is measured by simultaneous OH LIF and two-photon CO LIF. The product of the two LIF signals is proportional to the reaction-rate when the appropriate combination of LIF excitation schemes is used. The temperature and fuel concentration are measured using simultaneous polarized and depolarized Rayleigh scattering. Mixture fraction is determined by a three-scalar technique that combines the depolarized/polarized Rayleigh measurements with CO LIF. Two components of scalar dissipation are obtained from the mixture-fraction images. This technique offers improvements over two-scalar methods, which suffer from decreased sensitivity around the stoichiometric contour and biases in fuel-rich regions due to parent-fuel loss.

Both systems have been used to study the scalar structure of a piloted CH_4/air jet flame (Sandia flame D), which is shown in Figure 3 (center) and is a primary target for the International Workshop on

Measurement and Computation of Turbulent Nonpremixed Flames (TNF). Results from each lab were reported at the Twenty-ninth Combustion Symposium.

Results for the average H_2O mass fraction measured at the stoichiometric value of mixture fraction and conditioned upon the local, instantaneous value of the radial component of scalar dissipation are shown as symbols in Figure 3. At high-scalar dissipation (fast mixing), the H_2O mass fraction drops off dramatically, indicating local extinction of the flame. The curve represents a quasi-analytical expression for an S-shaped extinction curve for a single-step reaction, which has been fit to the data as a visual aid. A feature of piloted flames is that localized extinction occurs with increasing probability as the fuel jet velocity is increased. In flame D, the probability of local extinction is low, but the data clearly reveal the effect of scalar dissipation on the approach toward extinction.

Figure 3 (right) shows an example of two-dimensional measurements of the mixture fraction, temperature, scalar dissipation, OH and CO LIF, and reaction

rate. Near the centerline, regions of cold turbulent fuel are apparent. The regions of high-scalar dissipation form thin strips that bracket a zone of high-reaction rate. The combined imaging diagnostics link the $\text{CO} + \text{OH}$ reaction rate with the mixing field that controls it.

The two techniques described are complementary in the scalar dissipation results they produce and in their correlation with other measured quantities. They are also complementary in the sense that data from each can be used to refine the other and quantify uncertainties in the combined measurements. Detailed multiscalar point or line measurements are needed to develop and evaluate the algorithm used to determine mixture fraction from images. The two-dimensional three-scalar technique can achieve better spatial resolution in the mixture-fraction measurement than the one-dimensional Raman technique, which facilitates investigation of the effects of spatial averaging. Future work will include measurements in a series of turbulent jet and bluff-body flames that are also targets of the TNF Workshop series.

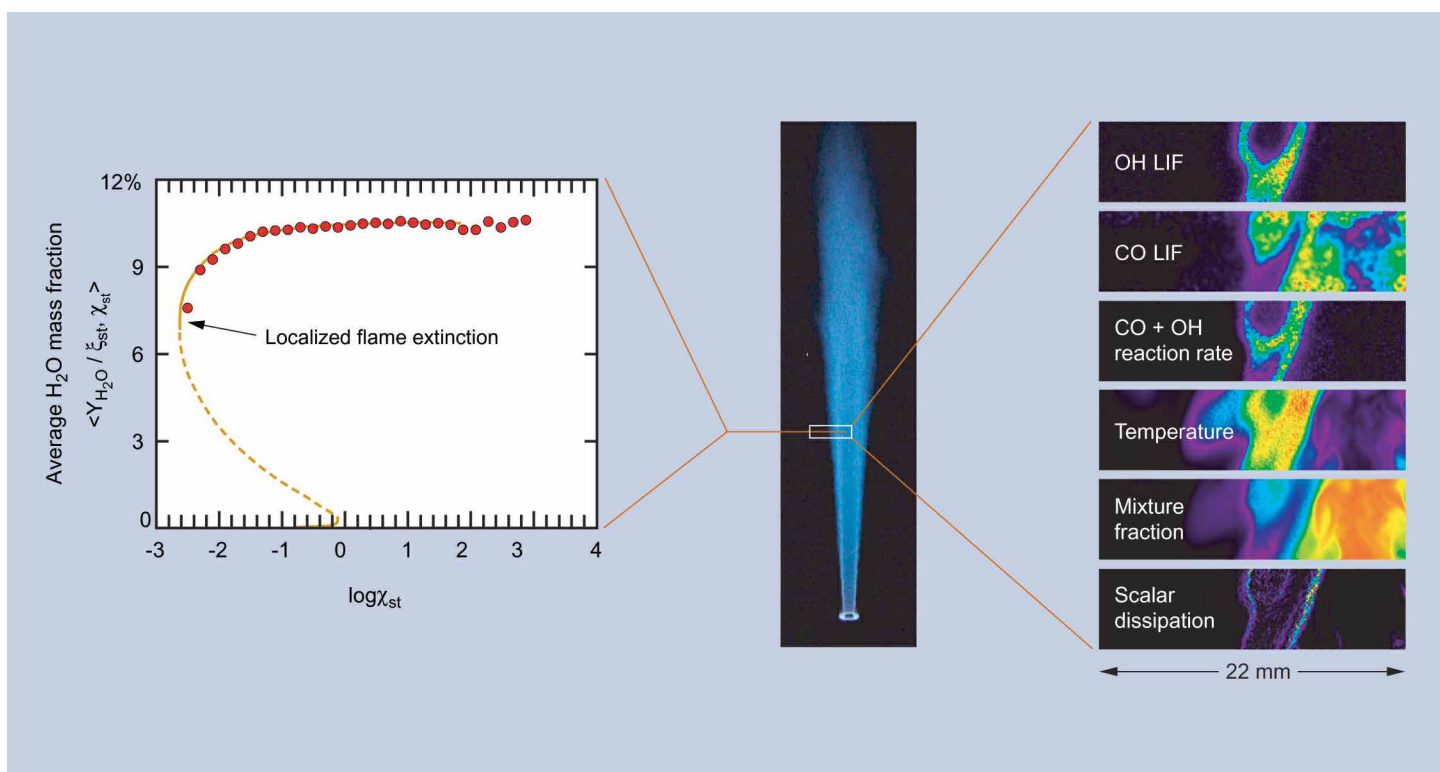


Figure 3. Measurements of piloted CH_4/air flame D (center) yield the average H_2O mass fraction shown as red circles at the stoichiometric mixture fraction, conditioned on the value of the local, instantaneous scalar dissipation, χ_{st} (left). Simultaneous images of OH LIF, CO LIF, reaction rate, temperature, mixture fraction, and scalar dissipation rate are shown in the right panel.



Glass Conference

Sandia hosted the Annual Review of DOE's Glass program at its Combustion Research Facility from September 9-11, 2002. The 70 attendees included representatives from U.S. industry, academia, and several national laboratories. A total of four Sandia projects ranging from flat glass coatings to emissions control research were included in the review. In addition to the presentations and technical discussions at the CRF, attendees spent a day touring the three Bay Area National Laboratories to view related research activities.



Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000

Sandia National Laboratories
Mail Stop 9056
P.O. Box 969
Livermore, California 94551-0969
<http://www.ca.sandia.gov/CRF/>

TEMP - RETURN SERVICE REQUESTED



PRESORTED
FIRST CLASS
U.S. POSTAGE
PAID
MODESTO, CA
PERMIT NO. 16

Combustion Research Facility NEWS



Adams and Bastress Awards Given to CRF Staff Members for 2000 and 2001

In September, Adams and Bastress Awards were presented to CRF staff members for 2000 and 2001. The O.W. Adams Award, named after Bill Adams, DOE's original CRF sponsor, was established in 1986 and is given each year to Sandians who have made exemplary research contributions.

The 2000 Adams Award recognizes Rob Barlow for his research in fundamental combustion measurements and technical leadership in establishing the highly successful International Turbulent Nonpremixed Flame (TNF) Workshop. Carl Hayden, Adams Award winner for 2001, was cited for his development of the coincidence photoion/photoelectron imaging technique and its use in the study of photodissociation dynamics of small molecules.

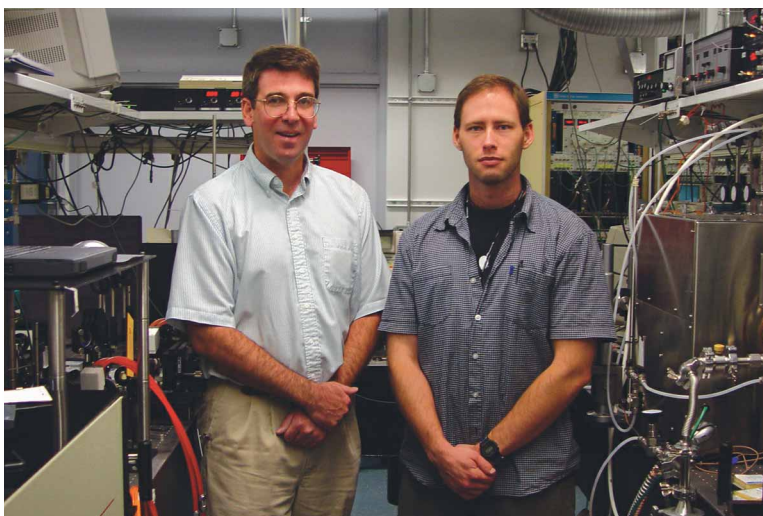
Dedicated to the memory of Dr. Karl E. Bastress, who guided early combustion research activities for DOE, the Bastress Award recognizes the Sandians whose exceptional contributions have led to a strong and effective coupling of CRF conservation-related programs to the needs of U.S. industry.

The 2000 Bastress Award was given to the team of Tom Kulp, Marshall Lapp, John Goldsmith, Scott Bisson, and Karla Armstrong in recognition of their work in developing short-and long-range remote sensing in environments of industrial and national importance.

Bob Green received the 2001 Bastress Award for his long-standing commitment to domestic engine manufacturers, highlighted by his measurements of transient exhaust gas recirculation (EGR) in engines. His infrared laser diagnostic provided industry with its first data on transient EGR distributions in engines.

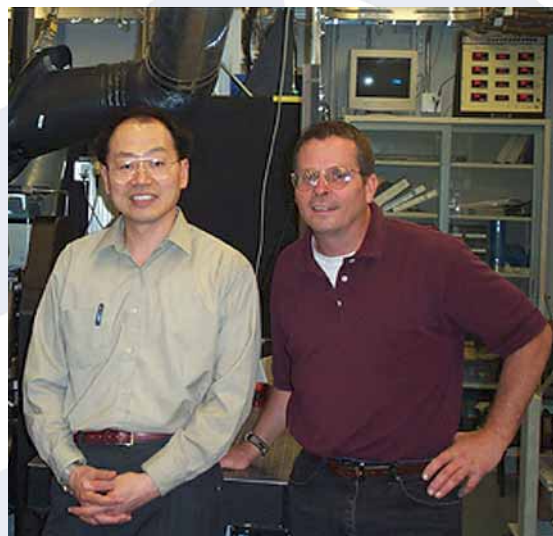


Bastress Award winners for 2000, (top left to right) Scott Bisson, Marshall Lapp, Tom Kulp, Karla Armstrong, and John Goldsmith were recognized as a team for developing new sensing technology for use in environments of industrial and national importance. Lower left, Jay Keller, Co-Manager of the Engine Combustion Department presents Bob Green with the 2001 Bastress Award for his work in measuring the distribution of recirculated exhaust gas in an engine. Lower right, Adams Award recipients Carl Hayden (2001) and Rob Barlow (2000) hoist the Adams plaque in the CRF lobby. Hayden was cited for his studies of the photodissociation dynamics of small molecules and Barlow for making and compiling fundamental combustion measurements.



Professor Jeffrey A. Gray of Ohio Northern University (left) returned to the CRF in August to collaborate with Tom Settersten in the Picosecond Diagnostics Laboratory. During this visit, Jeff, Tom, and Brian Patterson (right) used time-resolved laser-induced fluorescence to measure species- and temperature-dependent cross sections for the electronic quenching of $\text{NO A}^2\Sigma^+ (v=0)$ for temperatures ranging from 295–1300 K. Brian recently accepted a full-time position as a technologist at the CRF and will continue to work on experiments in the Picosecond Diagnostics Laboratory.

People



Professor Ming-Chia Lai (left) from Wayne State University recently completed a summer sabbatical leave in the high-speed direct-injection diesel engine laboratory, where he worked with Paul Miles (right) to clarify the sources of turbulence generation in swirl-supported diesel engines.

Post Docs Leave CRF for new positions



Josh Taylor, John Hewson, and Scott Mason recently completed their postdoctoral appointments and left for new positions. Josh joined the CRF in April 2001 and worked with Steve Rice, Mark Allendorf, and Tony McDaniel to implement a new method of studying the high-temperature kinetics associated with innovative approaches to catalytic partial oxidation. Josh recently took a staff position at the National Renewable Energy Laboratory's Center for Transportation Technologies and Systems. John worked with Alan Kerstein, first as a postdoc and then as a limited-term employee, on turbulent combustion modeling. He performed modeling studies of flames measured in the Turbulent Combustion Laboratory, and he developed a novel approach for modeling the performance of homogeneous-charge compression-ignition engines. John recently moved to a permanent staff position in Sandia's Fire Science and Technology Department in New Mexico, where he is performing modeling studies in support of fire safety programs. Scott recently joined Lockheed Martin after completing a postdoctoral appointment in the Reacting Flow Research Department at the CRF. During his tenure at Sandia, Scott worked closely with Jackie Chen, Chris Kennedy, and James Sutherland on development of an extensible, scalable MPP F90 direct numerical simulation code and on error controllers for time integration. Scott also worked on unsteady mixing effects on autoignition.

TNF6 Workshop Held in Sapporo

The Sixth International Workshop on Measurement and Computation of Turbulent Nonpremixed Flames (TNF6) was held in Sapporo, Japan this past July, just before the Twenty-ninth Combustion Symposium. Sixty-four researchers from twelve countries attended the three-day specialist meeting, which was hosted by Professors Yuji Ikeda of Kobe University and Masashi Katsuki of Osaka University. The TNF Workshop series is coordinated by Rob Barlow of Sandia's Reacting Flow Research Department. Proceedings and other information are available at <http://www.ca.sandia.gov/tdf/Workshop>.

The CRF News is Published bimonthly by the Combustion Research Facility, Sandia National Laboratories, Livermore, California, 94551-0969.

Director: William J. McLean, Mail Stop 9054

Editors: Howard Lentzner, Email: hlentz@sandia.gov
Jessica Matto

Graphic Artist: Daniel Strong

New Multiscalar Diagnostics Probe Turbulent Flames

Multiscalar laser diagnostics are providing new insights into scalar dissipation and its correlations with flow structure, species concentrations, reaction rate, and local extinction in turbulent flames. The development of predictive models for combustion systems depends upon an understanding of the fundamental interactions of flow dynamics, molecular transport, and chemical kinetics as well as accurate measurements of the quantities to be modeled. Scalar dissipation, which indicates the local rate of molecular mixing, is a central concept in models for non-premixed and partially premixed turbulent flames, making its measurement a high-priority target for experiments. However, scalar dissipation is hard to determine, especially in hydrocarbon flames, because it must be derived from simultaneous measurements of temperature and the mixture-fraction gradient. These types of measurements are underway in two CRF laboratories.

In the Turbulent Combustion Laboratory Rob Barlow, Adonios Karpetsis, Bob Harmon, and Matt Boisselle have combined line imaging of Raman scattering, Rayleigh scattering, and two-photon laser-induced fluorescence (LIF) of CO to obtain simultaneous measurements of temperature and all the major species. Mixture fraction is calculated directly from the major species mass fractions, and a component of scalar dissipation is determined from the mixture-fraction gradient along the measured line. Precise Raman-scattering measurements are obtained by combining an unintensified CCD camera with a high-speed, rotating shutter and using the energy of four pulsed Nd:YAG lasers. As shown in Figure 1, LIF imaging of OH is used to determine the instantaneous orientation and curvature of the flame as it intersects the multiscalar line.

In the Advanced Imaging Laboratory, Jonathan Frank and Ron Sigurdsson, in collaboration with visitors Marshall Long and Sebastian Kaiser from Yale University, have demonstrated simultaneous two-dimensional measurements of three scalars: reaction rate, mixture

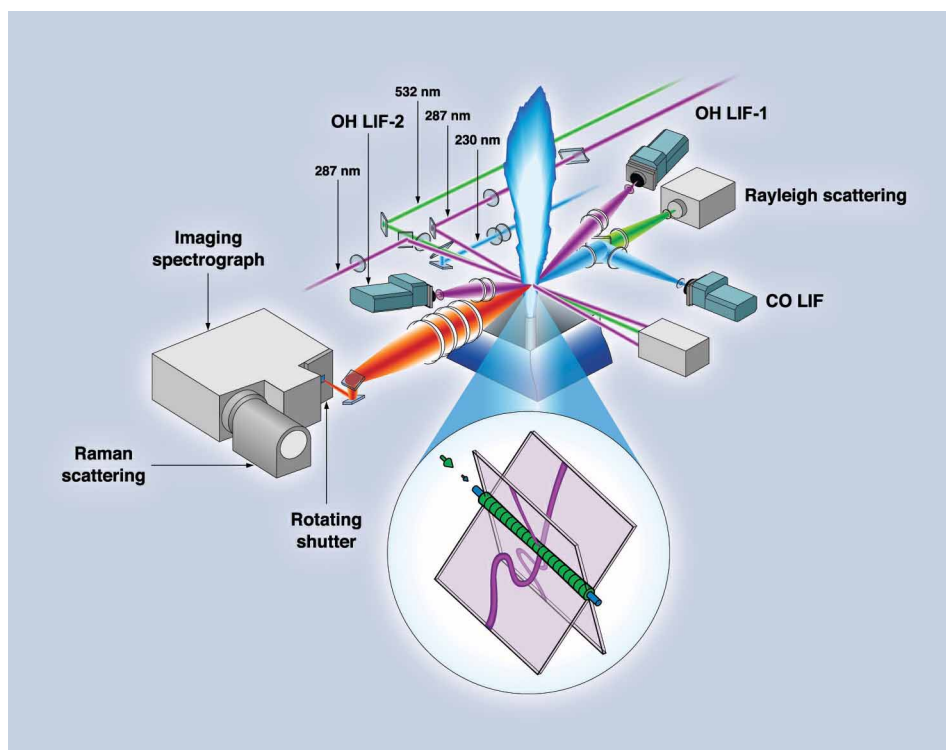


Figure 1. Schematic of the setup used in the Turbulent Combustion Laboratory to measure scalar dissipation. In this experiment, the mixture fraction is determined from the Raman/Rayleigh/CO-LIF measurements, and a component of scalar dissipation is calculated from the mixture fraction gradient. Inset illustrates the use of OH imaging in cross planes to determine flame orientation and curvature.

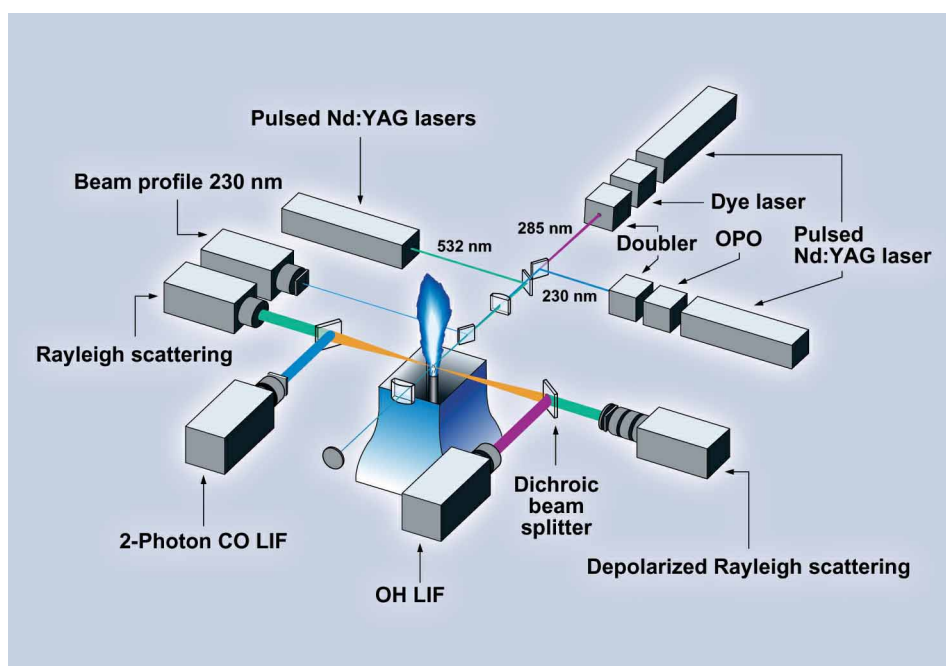


Figure 2. The apparatus for multiscalar, two-dimensional imaging in the Advanced Imaging Laboratory is used to simultaneously measure polarized and depolarized Rayleigh scattering, OH LIF, and two-photon CO LIF. These measurements are used to determine reaction rate, temperature, fuel concentration, mixture fraction, and two components of scalar dissipation.